Chapter 4.   The Kinetic Theory of Solids

1.   Determination of the Mean Radius of the Atom r_o

In this chapter the equation of state for a transition metal is derived. It is assumed that every atom in a transition metal, except those on the surface, are in a face centered configuration, that is, every atom in the interior is in contact with 6 atoms and only 6 atoms to which it is immediately adjacent. It is shown in chapter 5 that if an atom is in face centered configuration, then at room temperature it is bonded by the atomic field to the 6 atoms and only to the 6 atoms to which it is in contact. That is, at room temperature the absolute value of the potential energy between a given atom and an atom that it is in contact with, is greater than the sum of the kinetic energies of the two atoms. Also, at room temperature the absolute value of the potential energy between a given atom and an atom that it is not in contact with, is less than the sum of the kinetic energies of the two atoms.
The method developed however can be used to derive an equation of state for crystalline solids, such as quartz, in which every atom is in contact with and bonded to less than six atoms.
Equations of state are of theoretic importance as the bulk moduli are derived by taking partial derivatives of the pressure with respect to an extensive variable: e.g. In the case of a gas, $C_s^2 = (\frac{\partial P}{\partial \rho})_s$ where C_s is the adiabatic speed of sound in the gas, and s is the entropy.
Consider a transition metal at rest in inertial frame S. Let r_o be the mean radius of the atoms in the transition metal solid and let d, see figure 4.1, be the mean center to center distance of two adjacent atoms and let R be the mean separation distance between two adjacent atoms at absolute temperature T^oK and applied external pressure P_e.
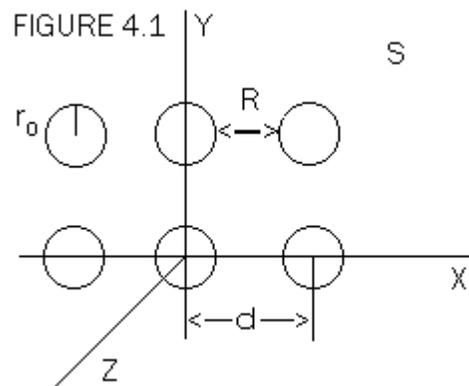

FIGURE 4.1

From figure 4.1

4.1 $d = 2r_o + R$

It is assumed that:

1) $P_e << \bar{P}_{int}$. The applied external pressure is much smaller than the average internal pressure where average internal pressure is the average pressure that two bound adjacent metal atoms exert on each other in the presence of an external pressure of one atmosphere.

2) To three significant figures, r_o remains constant on the interval $0<T<T_{melt}{}^oK$.

3) $d=d(T,P_e)$ and $R=R(T,P_e)$ with special case $d(0,P_e)=2r_o$ and $R(0,P_e)=0$. The special case $R_o(T)$ is defined as $R_o(T) \equiv R(T, 10^6 \text{ dy/cm}^2)$ i.e. $R_o(T)$ is determined at an external pressure of $P_e=10^6 \text{ dy/cm}^2=1$ atms.

The atomic field force between two atoms is given by:

$$4.2 \qquad \underset{\sim}{f}_{12} = -\frac{\partial \Phi_{12}}{\partial r}\hat{r}_{21} , \quad \Phi_{12} = \int_{V_1} \rho_1^*(h)\Psi_2(S)dV_1 , \quad S^2=d^2+h^2-2dh\cos\phi$$

Where $\underset{\sim}{f}_{12}$ is the force that atom #2 exerts on atom #1 and $\hat{r}_{21}$ is a unit vector from atom #2 to atom#1, see figure 4.2 , and Φ_{12} is the potential energy of atoms #1 and #2.

FIGURE 4.2
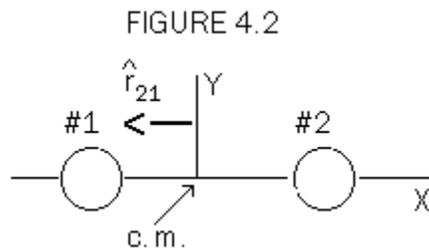
Each atom is considered at the center of a cube of side d. The density of the material ρ is:

$$4.3 \qquad \rho=m/ d^3 \quad \text{and} \quad d= [m/\rho]^{1/3} \quad \text{where m is the mass of the atom.}$$

The solid is held together by bond forces of form 4.2 and the individual atoms are kept apart at a mean distance d by elastic collisions. The collisions result in an instantaneous pressure P(t) exerted on each atom, the average pressure of which is calculated in section three. As T^oK approaches 0^oK, the average kinetic energy of each atom approaches 0 ergs. i.e. $\lim_{T->0^oK} KE(T) -> 0$ ergs ; The atoms come to rest with respect to one another and $\lim_{T->0^oK} R(T) -> 0$ cm. 4.3 becomes:

$$4.4 \qquad r_o =\tfrac{1}{2}[m/\rho(0)]^{1/3}$$

The temperature of a solid or a liquid should be measured by placing an inert gaseous element in thermal equilibrium with the solid or liquid, and measuring the U_{rms} speed of the gas. T is then calculated using the defining relation, $\frac{1}{2}mU_{rms}^2 = \frac{3}{2}KT$, where m is the mass of a molecule of the gas. In the following, except for measurements made with a mercury thermometer, all published temperature measurements (e.g. melting point, boiling point) should be considered suspect until measured using the defining relation. However for the purpose of exposition, temperature measurements will be used as published.

The density of the transition metals as a function of temperature has been measured, see reference 4.1, to three significant figures by measuring the linear dimensions of a rod of known mass on the interval $5.0^{\circ}K \approx T < T_M$. r_0 to three significant digits is: $r_0 = \frac{1}{2}[m/\rho_0(0)]^{1/3} = \frac{1}{2}[m/\rho_0(5.0)]^{1/3}$. The zero subscript on ρ indicates that ρ is measured with $P_e = 1$ atms. The following densities are taken from reference 1, chapter 4.

a) $\rho_0(0^{\circ}K)_{Fe} = 7.91 gm/cm^3$ and using 4.4 $(r_0)_{Fe} = 1.13 \overset{o}{A}$

b) $\rho_0(0^{\circ}K)_{Cu} = 9.04 gm/cm^3$ $(r_0)_{Cu} = 1.13 \overset{o}{A}$

c) $\rho_0(0^{\circ}K)_{Al} = 2.73 gm/cm^3$ $(r_0)_{Al} = 1.27 \overset{o}{A}$

2. Determination of $R_0(T)$ with $P_e = 1$ atms

Let L(T) be the length of a transition metal rod at $T^{\circ}K$ with $P_e = 1$ atms and define $\frac{\Delta L(T)}{L_0} \equiv \frac{L(T) - L(293)}{L(293)}$ where $L_0 \equiv L(293)$ is the length of the rod at $293^{\circ}K$. $\frac{\Delta L(T)}{L_0}$ has been experimentally determined and is listed in r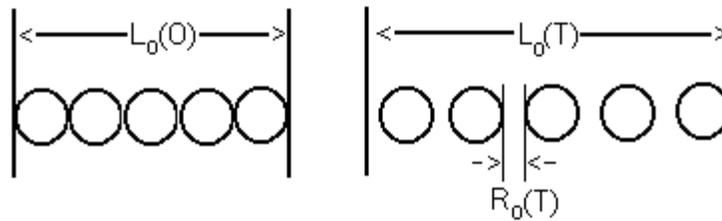eference 1, chapter 4, p254 etc. Note that: In reference 4.1, $\frac{\Delta L(T)}{L_0}$ is listed as a %. $\frac{\Delta L(T)}{L_0}$ is in general a monotonically increasing function on the interval $5.0^{\circ}K = T < T_M$. For those transition elements with melt temperature $T_M > 10^{3} {}^{\circ}K$ and in the temperature range $5.0^{\circ}K \leq T \leq 10^{3} {}^{\circ}K$:

From table 4, $(.86)10^{-3} \leq |\frac{\Delta L(T)}{L_0}| \leq (1.74)10^{-2}$.

Let N_A be the number of atoms along the length of the rod: L(T) becomes,
$L(T) = N_A[2r_0 + R_0(T)]$. See figure 4.3 .

FIGURE 4.3

$\frac{\Delta L(T)}{L_o}$ becomes: $\frac{\Delta L(T)}{L_o} \equiv \frac{L(T)-L(293)}{L(293)} = \frac{R_o(T)-R_o(293)}{2r_o+R_o(293)}$. Solving for $R_o(T)$ with $R_o(0)=0$ and

$\frac{\Delta L(0)}{L_o} \approx 10^{-3}$ yields, $R_o(T) = \frac{2r_o}{1+\frac{\Delta L(0)}{L_o}}[\frac{\Delta L(T)}{L_o} - \frac{\Delta L(0)}{L_o}] \doteq 2r_o[\frac{\Delta L(T)}{L_o} - \frac{\Delta L(0)}{L_o}][1-\frac{\Delta L(0)}{L_o}]$.

But $|\frac{\Delta L(T)}{L_o}| << 1$ and consequently $|\varepsilon_1| << 1$ and $|\varepsilon_2| << 1$ where $\varepsilon_1 \equiv [\frac{\Delta L(T)}{L_o} - \frac{\Delta L(0)}{L_o}]$

and $\varepsilon_2 \equiv \frac{\Delta L(0)}{L_o}$. Therefore:

$R_o(T) = 2r_o[\frac{\Delta L(T)}{L_o} - \frac{\Delta L(0)}{L_o}][1-\frac{\Delta L(0)}{L_o}] = 2r_o\varepsilon_1(1-\varepsilon_2) \doteq 2r_o\varepsilon_1$

For future reference:

$$4.5 \qquad R_o(T) = 2r_o[\frac{\Delta L(T)}{L_o} - \frac{\Delta L(0)}{L_o}] \quad \text{With special case:} \quad R_o(293) = -2r_o\frac{\Delta L(0)}{L_o}$$

This formula will be used in section four for determining the speed of sound in the transition metals. $\frac{\Delta L(0)}{L_o}$ will be evaluated as if $\frac{\Delta L(0)}{L_o} = \frac{\Delta L(5)}{L_o}$.

Table 4.1 below lists:

1) r_o: where r_o is determined using 4.4,

2) $\frac{\Delta L(5)}{L_o}$ and $\frac{\Delta L(10^3)}{L_o}$: where $\frac{\Delta L(5)}{L_o}$ and $\frac{\Delta L(10^3)}{L_o}$ are determined from reference 1, chapter 4.

3) $R_o(293)$ and $R_o(10^3)$: where $R_o(293)$ and $R_o(10^3)$ are determined using 4.5.

A sample calculation follows. From above $2(r_o)_{Fe} = 2.26 \, \overset{o}{A}$. From reference 1, chapter 4: $\frac{\Delta L(5)}{L_o}_{Fe} = -(2.04)10^{-3}$. From 4.5: $R_o(293)_{Fe} = -2r_o\frac{\Delta L(5)}{L_o}_{Fe} = (2.26)10^{-8}(2.04)10^{-3} = (4.61)10^{-11}$cm.

The transition elements are listed in order of increasing atomic mass.

Table 4.1

| Element	r_0 Å	$-\dfrac{\Delta L(5)}{L_0}10^3$	$R_0(293)\ 10^{11}$cm	$\dfrac{\Delta L(10^3)}{L_0}10^3$	$R_0(10^3)\ 10^{11}$cm
Mg	1.42	4.59	13.0	Melt	
Al	1.27	4.18	10.6	Melt	
Ti	1.30	1.53	3.98	7.36	23.1
Fe	1.13	2.04	4.61	10.7	28.7
Ni	1.11	2.31	5.13	11.3	30.2
Cu	1.13	3.24	7.32	13.7	38.2
Zn	1.23	6.82	16.8	Melt	
Mo	1.30	.92	2.39	3.85	12.4
Ag	1.29	4.1	10.6	15.7	51.1
Sn	1.50	4.68	14.0	Melt	
W	1.25	.86	2.15	3.39	10.6
Pt	1.25	1.92	4.76	6.99	22.1
Au	1.28	3.27	8.37	11.5	37.9
Pb	1.55	7.08	21.9	Melt	
U	1.38	2.56	7.07	17.4	55.2

The "Melt" in the table stands for elements at which melt has occurred below 10^3 ^{0}K and for which $\dfrac{\Delta L(10^3)}{L_0}$ has not been measured. For visual evidence in support of the contention that $R_0(293^0K)<<r_0$ see reference 2, chapter 4 .

3.   Equation of State for the Transition Elements

Consider two adjacent solid mass atoms bonded together as in figure 4.4. With an external pressure of 1 atmosphere, every atom in the interior of the solid is confined to a volume of $[2r_0+R_0(T)]^3$.
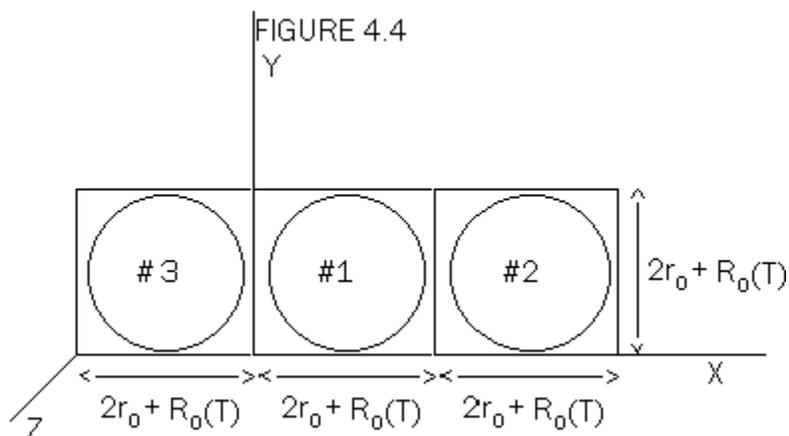
FIGURE 4.4

The average pressure P_0 due to collisions between atom #1 and atom #2 in figure 4.4 is calculated below. The classical thermo dynamical derivation of $P = 1/3\rho U_{rms}^2$ for an ideal gas, serves as a model for the derivation of the internal pressure in a transition metal, taking into account the atomic field force 4.2 between neighboring atoms, the finite radius of the atom r_0 and the fact that in a solid, a given atom always collides with the same neighboring atoms.

With $\frac{1}{2}mU_{rms}^2 = \frac{3}{2}KT$, it is assumed that the solid is in thermal equilibrium with its surroundings and that therefore there is no net energy flow within the solid. Let U_x be the time average of the absolute value of the x component of velocity of atom #1, averaged over the time it takes atom #1 to travel from its collision point with atom #2 to its collision point with atom #3 and back to its collision point with atom #2. In general $U_x = U_x(t_i)$ where t_i , i=1,2,3,...represents the times at which atom #1 collides with atom #2. In the following, t_i will be treated as if it were a continuous variable.

The average pressure P between atoms #1 and #2 is calculated as if both atoms at collision have the same speed $U_x(t)$ and opposite momentum. This is permissible as by assumption there is no net energy flow within the solid. For every collision C between #1 and #2 with initial kinetic energy and momentum, $KE_{1_{in}}$, $\underset{\sim}{P}_{1_{in}}$, $KE_{2_{in}}$, $\underset{\sim}{P}_{2_{in}}$, collision C is treated as if, $KE_{1_{in}} = KE_{2_{in}}$ and $\underset{\sim}{P}_{1_{in}} = -\underset{\sim}{P}_{2_{in}}$. After separation,

$KE_{1_{out}} = KE_{2_{out}}$ and $\underset{\sim}{P}_{1_{out}} = -\underset{\sim}{P}_{2_{out}}$ where $KE_{1_{in}} = KE_{2_{in}} = KE_{1_{out}} = KE_{2_{out}} = \frac{3}{2}KT$ and $\underset{\sim}{P}_{1_{in}} = -\underset{\sim}{P}_{1_{out}} = -\underset{\sim}{P}_{2_{in}} = \underset{\sim}{P}_{2_{in}}$. The net effect is to treat every collision as if #1 reflected from #2 and #2 reflected from #1.

Let R(t,T) represent the x component of the distance that atom #1 travels, from the time that atom #1 is in contact with atom #2 to the time that atom #1 is in contact with atom #3. $\overline{R(t,T)} = R(T)$.

Let Δt represent the time interval from the instant that atom #1 is in contact with atom #2 until the instant that atom #1 is again in contact with atom #2: $\Delta t = 2\dfrac{R(t,T)}{U_x(t)}$. The solid has volume V and contains N atoms and therefore $V = N[2r_0 + R_0(T)]^3$. With $\frac{1}{3}U_{rms}^2 = \overline{U_x^2}$, P becomes:

$$P = [\overline{\frac{\Delta m U_x}{\Delta t \Delta A}}] = \frac{2m}{\Delta A}[\overline{\frac{U_x \cdot}{\Delta t}}] = \frac{m}{\Delta A}[\overline{\frac{U_x^2}{R(t,T)}}] = \frac{m}{\Delta A}[\frac{\overline{U_x^2}}{R(t,T)}] = \frac{1}{3}\frac{m}{\Delta A}[\frac{U_{rms}^2}{R(T)}] = \frac{1}{3}m\frac{U_{rms}^2[2r_0 + R(T)]}{R(T)[2r_0 + R(T)]^3} = \frac{NKT[2r_0 + R(T)]}{R(T)V}$$

and $PV = \dfrac{NKT[2r_0 + R(T)]}{R(T)} = \dfrac{2r_0 NKT}{R(T)}[1 + \dfrac{R(T)}{2r_0}]$. Let $P_0(T)$, $R_0(T)$, $V_0(T)$ and $\rho_0(T)$ represent the values of their respective variables evaluated at 1 atm. external pressure.

$P_0 V_0 = \dfrac{2r_0 NKT}{R_0(T)}[1 + \dfrac{R_0(T)}{2r_0}]$. Also $P_0 = \dfrac{P_0 KT[2r_0 + R_0(T)]}{mR_0(T)} = \dfrac{2r_0 \rho_0 KT}{mR_0(T)}[1 + \dfrac{R_0(T)}{2r_0}]$. Although P_0

is computed using atoms #1 and #2, the same results hold for atom #1 and any atom in the y and z direction to which atom #1 is bonded.

The average contact force $\overline{\underset{\sim}{f}}_{C_{21}}$ of atom #1 acting on atom#2 is $\overline{\underset{\sim}{f}}_{C_{21}} = P_0(2r_0)^2 \hat{x}$

with $\overline{\underset{\sim}{f}}_{C_{12}} = -P_0(2r_0)^2 \hat{x}$. The average field force 4.2, of atom #1 acting on atom#2 is

$\overline{\underset{\sim}{f}}_{21} = -P_0(2r_0)^2 \hat{x}$ with $\overline{\underset{\sim}{f}}_{12} = P_0(2r_0)^2 \hat{x}$ and therefore $\overline{\underset{\sim}{f}}_{21} = -\overline{\underset{\sim}{f}}_{C_{21}} = -\overline{\underset{\sim}{f}}_{12} = \overline{\underset{\sim}{f}}_{C_{12}}$

Compiling results:

4.6 $\quad P_0 V_0 = \dfrac{2r_0 NKT}{R_0(T)}[1 + \dfrac{R_0(T)}{2r_0}]$ and $P_0 = \dfrac{2r_0 \rho_0 KT}{mR_0(T)}[1 + \dfrac{R_0(T)}{2r_0}]$ Equation of State, Transition metal

$\qquad PV = NKT \qquad$ and $\quad P = \dfrac{\rho KT}{m}$ Equation of State, Ideal Gas, $R_0(T) \gtrsim r_0$

$\qquad \overline{\underset{\sim}{f}}_{21} = -\overline{\underset{\sim}{f}}_{C_{21}} = -\overline{\underset{\sim}{f}}_{12} = \overline{\underset{\sim}{f}}_{C_{12}} \qquad$ Negative Equality Between Time Averaged Field Force and Contact Force

Let $mU_{x_C}\hat{x}$ represent the x component of momentum of atom #1 at the instant that atoms #1 and #2 are first in contact. See figure 4.4 . Let Δt_C represent the time from the instant that atoms #1 and #2 are first in contact until entire atom #1 has reflected from atom #2 and has momentum $-mU_{x_C}\hat{x}$. In the derivation of 4.6 it is

tacitly assumed that $2\overline{\Delta t_C} << \overline{\Delta t}$ where $\overline{\Delta t}$ is the average down and back time.

Consequently: $2\overline{\Delta t_C}/\overline{\Delta t} = 2\overline{U}_x \overline{\Delta t_C}/2R_0(T) = [\dfrac{KT}{2\pi m}]^{\frac{1}{2}} \overline{\Delta t_C}/R_0(T) << 1$ and therefore

$\overline{\Delta t_C} << R_0(T)/[\dfrac{KT}{2\pi m}]^{\frac{1}{2}}$. This hypothesis is examined in section seven.

Using table 4.1 and T=293^{0}K for Fe: $\overline{\Delta t_{C_{Fe}}} << (4.61)10^{11}[2\pi m]^{1/2}/[KT]^{1/2} =$

$(4.61)10^{-11}(2.42)10^{-11}/(2.01)10^{-7} = (5.5)10^{-15}$.

Requiring $\overline{\Delta t_{C_{Fe}}}$ to be one order of magnitude smaller than or equal to $(5.5)10^{-15}$:

$\overline{\Delta t_{C_{Fe}}} \leq (5.5)10^{-16}$sec. Let $\overline{V}_{C_{Fe}}$ be the average speed of a compressional wave through the solid mass Fe atom as generated by atom atom collisions:

$\overline{V}_{C_{Fe}} = 2r_0/\overline{\Delta t_{C_{Fe}}} \geq (2.2)10^{-8}/(5.5)10^{-16} = (4.0)10^{+7}$cm/sec.

Returning to 4.6 to evaluate it for Fe at 293^{0}K using table 4.1:

4.7 $\qquad P_0 = KT\{/[R_0(T)][2r_0 + R_0(T)]^2\} \doteq \{KT/4(r_0)^2 R_0(T)\}[1 - R_0(T)/r_0]$

$\qquad\qquad P_{0_{Fe}} \doteq [(4.04)10^{-14}/(2.36)10^{-26}][1.00]$

$\qquad\qquad P_{0_{Fe}} \doteq (1.7)10^{12}dy/cm^2 = (1.7)10^6$atm.

Similar results hold for the other transition metals. $P_{0_{Fe}}$ is the average pressure that Fe atoms exert on one another, when subjected to an external pressure of one atmosphere. The large pressure is due to the high atomic collision rate $\approx 10^{15}$/sec which in turn is due to small mean free path $R_0(293) \approx 10^{-11}$cm. and small average turn around collision time $\overline{\Delta t_c} \leq (5.5)10^{-16}$sec. See chapter 4, section 7.

The pressure P_G exerted on matter at the center of the earth due to the gravitational field of the earth is order of magnitude equivalent to the average pressure that atoms exert on one another in a transition metal at T=293^{0}K and one atmosphere external pressure , i.e. $P_G \approx P_0 \approx 10^{12}$dy/cm^2= 10^6atm where P_G at the center of the earth is due to the gravitational field of the earth and P_0 of the transition metals is due to the atomic field of the atom.

The striking similarity of $P_{0_{Fe}}$ =(1.7) 10^{12}dy/cm^2 and the experimentally determined isothermal bulk modulus for Fe at 293 ^{0}K of (1.7)10^{12} dy/cm^2 , reference 4, chapter 4, will be examined in section five.


4.   Incremental Pressure Difference $P_T(x,t)$

The speed of sound in the transition metals is order of magnitude 10^5cm/sec and that of a gas at STP, 10^4cm/sec. At first sight this is difficult to understand given that the U_{rms} of Pb at 1atm external pressure and 293 ^{0}K is $U_{rms}=(3KT/m)^{1/2}=$ (1.1) 10^3cm/sec with measured sound speed (2.0) 10^5cm/sec, while the U_{rms} of N_2 at 1 atm pressure and 293 ^{0}K is $U_{rms}=(3.0)$ 10^3cm/sec with measured sound speed (3.3) 10^4cm/sec . The U_{rms} of Pb is $\cong 1/3$ that of N_2 while the measured speed of sound in Pb is $\cong 7$ times that of N_2 at S.T.P.

The adiabatic speed of sound in gasses is given by $C_s = (\gamma \frac{dP}{d\rho})_s^{1/2}$ where γ is the ratio of the specific heats and s is the entropy. As will be derived below, the adiabatic speed of sound in the transition metals is:

4.8 $$C_s = \{ \frac{(C_p+3K) P_0}{C_p} \frac{P_0}{P_0} \}^{1/2}$$

Consider a transition metal solid in rectangular form of length l_0 and cross sectional area $\Delta A=H^2$, figure 4.5.

FIGURE 4.5
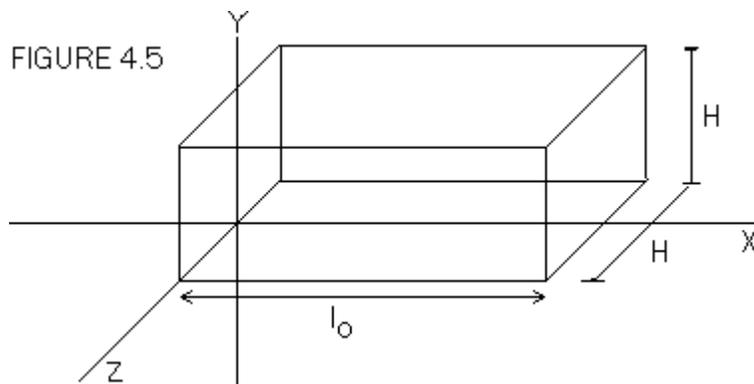
A transducer is bonded to the metal at x=0 and generates an oscillating pressure pulse $P_T=P_T(0, t)$ for t ≥0. This in turn generates a plane sound wave $P_T(x,t)$ traveling through the metal. A recording transducer is fixed to the metal at x=l_o. The metal is in a constant external atmospheric pressure of 1atm.=10^6 dy/cm^2 and the metal is fixed to inertial frame S. Inertial frame S is massive enough so that when the transducers are operating , the acceleration of the frame is effectively zero as measured by on board accelerometers. Effectively zero means that reducing the measured acceleration, by increasing the mass of the frame, does not change the measured sound speed.

Following the analysis in chapter two, x is independent of t and t is independent of x. Let $P_T(x,t)$ represent the total internal average pressure inside the metal at x at time t. In the absence of a sound field, $P_T(x,t)=P_o$. In the presence of a sound field, $P_T(x,t)=P_o+P_S(x,t)$ where $P_S(x,t)$ represents the overpressure due to the sound field..

All time averages concerning atom #1 are computed from the time atom #1 strikes atom #2, strikes atom #3 and then strikes atom#2 again. See figure 4.4. In the absence of a sound field, $\rho \equiv \rho_o$, $T \equiv T_o$ and $R_o(T) \equiv R_o(T_o)$. In the presence of a sound field ρ, T and R are variables dependent on the magnitude of the external pressure $P_e(x,t) =P_S(x,t)+ 10^6$ with $\rho=\rho(x,t)$, T=T(x,t) and $R_x=R_x(x,t)$ where $2r_o+R_x(x,t)$ is the separation distance between the centers of atom #1 and the atom #2. The derivation of $P_T(x,t)$ is exactly the same as the derivation of $P_o(T)$ and results in replacing ρ_o by $\rho(x,t)$, T by T(x,t) and $R_o(T)$ by $R_x(x,t)$.

$P_e(x,t)$, $P_S(x,t)$, $P_T(x,t)$ and $P_o(T_o)$ are related by:

4.9 $P_e(x,t) =10^6 dy/cm^2=1atms.$, t<0

$P_e(x,t) =10^6 dy/cm^2$, t≥0, Ct ≤ x≤ l_o

$P_e(x,t) =P_S(x,t)+ 10^6$, t≥0, 0≤ x≤ Ct≤ l_o

$P_S(x,t) = P_T(x,t) - P_o(T_o)=\dfrac{2r_o\rho(x,t)KT(x,t)}{mR_x(x,t)}[1+\dfrac{R_x(x,t)}{2r_o}]-\dfrac{2r_o\rho_o KT_o}{mR_o(T_o)}[1+\dfrac{R_o(T_o)}{2r_o}]$,

For t≥0, 0≤ x≤ Ct≤ l_o : C≈ 10^5cm/sec .

Let $\Delta\rho=\rho(x,t)-\rho_0(T_0)$, $\Delta T=T(x,t)-T_0$, $\Delta R_x=R_x(x,t)-R_0(T_0)$, where ρ_0, T_0, R_0 are equilibrium values experimentally determined in the absence of a sound field at one atmosphere external pressure at temperature T_0. $\Delta R_x(x,t)$ represents the change in length of $R_0(T_0)$ in the x direction due to the sound wave traveling in the x direction Using 4.9, expand $P_S(x,t)$ around $\rho(x,t)=\rho_0(T_0)$, $T(x,t)=T_0$, $R_x(x,t)=R_0(T_0)$, this yields:

$P_S(x,t)=P_0[\frac{\Delta\rho}{\rho_0}+\frac{\Delta T}{T_0}-\frac{\Delta R_x}{R_0(T_0)}]+...$ An overpressure of $|P_S(x,t)|=10^6$dy/cm^2 is sufficient to flatten a wooden frame house and in general for most sound sources

$|P_S(x,t)| < 10^6$dy/cm$^2 << P_0 \approx 10^{12}$dy/cm^2 and $\frac{|P_S(x,t)|}{P_0} << 1$. If $\Delta R_x<0$, then $\Delta T>0$ and

$\Delta\rho>0$ and if $\Delta R_x>0$, then $\Delta T<0$ and $\Delta\rho<0$. With $|\frac{R_x(x,t)}{2r_0}|<1$, every term in the

expansion of $P_S(x,t)$ has the same sign and consequently $|\frac{\Delta\rho}{\rho_0}|<<1$, $|\frac{\Delta T}{T_0}|<<1$, and

$|\frac{\Delta R_x}{R_0(T_0)}|<<1$. Dropping higher order terms: $P_S(x,t)\doteq P_0[\frac{\Delta\rho}{\rho_0}+\frac{\Delta T}{T_0}-\frac{\Delta R_x}{R_0(T_0)}]$. In the

future, terms of the form $(1\pm\frac{R_x(x,t)}{2r_0})$ will be replaced by 1.

Expand $\rho=\frac{m}{(2r_0+R(x,t))^3}$ around $\rho_0=\frac{m}{(2r_0+R_0(T_0))^3}$ and evaluate $\frac{\rho-\rho_0}{\rho_0}$, this yields:

$|\frac{\Delta\rho}{\rho_0}|\equiv|\frac{\rho-\rho_0}{\rho_0}|=|\frac{\Delta V}{V}|$. During the compressive (expansive) phase, the sound wave increases (decreases) the total energy of atom #1 which then shares the energy increase (decrease) with the atoms in the y and z direction. This results in a creation of a ΔR_y and ΔR_z with $\Delta R_y=\Delta R_z$. If $\Delta R_x>0$ then $\Delta R_y=\Delta R_z<0$ and if $\Delta R_x<0$ then $\Delta R_y=\Delta R_z>0$ and if $\Delta R_x=0$ then $\Delta R_y=\Delta R_z=0$.

From section three, $\overline{f}_{ij} = -\overline{f}_{c_{ij}}$ and $\overline{f}\equiv|\overline{f}_{ij}|=|\overline{f}_{c_{ij}}|=P_0(2r_0)^2$.

Let ΔW represent the work done on atom #1 by the sound wave. Because of energy sharing $\frac{\Delta W}{3}=\overline{f}\Delta R_y=\overline{f}\Delta R_z=-\overline{f}\Delta R_x$ and consequently $\Delta R_y=\Delta R_z=-\Delta R_x$. The work ΔW

done on atom #1 is $\Delta W =-3\overline{f}\Delta R_x=-3P_0(2r_0)^2\Delta R_x=-3\frac{KT_0}{R_0(T_0)}\Delta R_x$

Expanding ΔV, $\Delta V=V-V_0(T_0)\doteq(2r_0)^3[1+R_y/r_0][1+R_x/2r_0]-(2r_0)^3[1+3R_0(T_0)/2r_0]=(2r_0)^2[2\Delta R_y+\Delta R_x]=-(2r_0)^2\Delta R_x$. If $\Delta R_x>0$ then $\Delta V<0$ and if $\Delta R_x<0$ then $\Delta V>0$.

Consequently, $|\frac{\Delta\rho}{\rho_0}|=|\frac{\Delta V}{V}|\doteq\frac{1}{2}|\frac{\Delta R_x}{r_0}|<<|\frac{\Delta R_x}{R_0(T_0)}|$ and using $|\frac{\Delta\rho}{\rho_0}|<<|\frac{\Delta R_x}{R_0(T_0)}|$ in the

above expression for $P_S(x,t)$ yields $P_S(x,t)=P_0[\frac{\Delta T}{T_0}-\frac{\Delta R_x}{R_0(T_0)}]$.

The adiabatic first law of thermodynamics:

$\Delta E = \Delta KE + \Delta PE = 3/2 K \Delta T + [C_p \Delta T - 3/2 K \Delta T] = \Delta W = -3\dfrac{KT_0}{R_0(T_0)}\Delta R_X$. Consequently

$C_p \Delta T = -3\dfrac{KT_0}{R_0(T_0)}\Delta R_X$ and $\dfrac{\Delta T}{T_0} = \dfrac{-3K\Delta R_X}{C_p R_0(T_0)} \approx -\dfrac{\Delta R_X}{R_0(T_0)}$. Note that for an ideal gas,

$\Delta W = -P_0 \Delta V$, however for a transition metal conducting a plane wave sound wave,

$\Delta W = -3P_0(2r_0)^2\Delta R_X \neq P_0(2r_0)^2\Delta R_X = -P_0 \Delta V$.

Substituting for $\dfrac{\Delta T}{T_0}$ in $P_S(x,t)$ above yields:

4.10 $P_S(x,t) = -P_0 \dfrac{(C_p + 3K)\Delta R_X(x,t)}{C_p}\dfrac{1}{R_0(T_0)} \approx -2P_0 \dfrac{\Delta R_X(x,t)}{R_0(T_0)}$

Referring to figure 4.5, let P_w (w/cm^2) represent the average power per unit area supplied to the metal by the transducer. The average power supplied to a given atom is $P_w(2r_0)^2$. In the following, order of magnitude estimates are made of $\left|\overline{\dfrac{\Delta R}{R_0(T_0)}}\right|$, $\left|\overline{\dfrac{P_S(x,t)}{P_0(T_0)}}\right|$, $\left|\overline{\dfrac{\Delta T}{T_0}}\right|$ and $\left|\overline{\dfrac{\Delta \rho}{\rho_0}}\right|$.

The average time $\overline{\Delta t}$ it takes sound energy to travel $2r_0$ cm is $\overline{\Delta t} = \dfrac{2r_0}{C} \approx \dfrac{10^{-8}}{10^5} = 10^{-13}$ sec. where C is the speed of sound in the metal. The average power flow across an area $(2r_0)^2$ is $P_w(r_0)^2 \approx \left|\dfrac{K\overline{\Delta T}}{\Delta t}\right|$ and $|\overline{\Delta T}| \approx \dfrac{P_w(r_0)^2 \overline{\Delta t}}{K} \approx 10^{-13}P_w$ and

$\left|\overline{\dfrac{\Delta T}{T_0}}\right| \approx \left|\overline{\dfrac{\Delta R}{R_0(T_0)}}\right| \approx \left|\overline{\dfrac{P_S(x,t)}{P_0(T_0)}}\right| \approx \dfrac{10^{-13}P_w}{T_0}$ and $\left|\overline{\dfrac{\Delta \rho}{\rho_0}}\right| \approx \left|\overline{\dfrac{\Delta R}{r_0}}\right| \approx \dfrac{R_0(T_0)}{r_0}\dfrac{10^{-13}P_w}{T_0} \approx$

$\dfrac{10^{-11}}{10^{-8}}\dfrac{10^{-13}P_w}{T_0} = \dfrac{10^{-16}}{T_0}P_w$. With $P_w = 0.1$w/cm$^2 = 10^6$erg/(sec cm^2) and $T_0 = 300^0$K:

$\left|\overline{\dfrac{\Delta \rho}{\rho_0}}\right| \approx 10^{-12}$, $\left|\overline{\dfrac{\Delta T}{100}}\right| \approx \left|\overline{\dfrac{\Delta R}{R_0(T_0)}}\right| \approx \left|\overline{\dfrac{P_S(x,t)}{P_0(T_0)}}\right| \approx 10^{-9}$ and $|\overline{\Delta T}| \approx 10^{-7}$K^0. With $P_0 = 10^{12}$dy/cm^2 , $|\overline{P_S(x,t)}| \approx 10^3$ dy/cm^2 and $|\overline{\Delta R}| \approx 10^{-20}$cm .

Compiling the order of magnitude estimates of the quantities computed above for $T_0 = 300^0$K :

4.11   With zero power input: $P_0(T_0) = 10^{12}$dy/cm^2, $\left|\overline{\dfrac{P_S(x,t)}{P_0(T_0)}}\right| = |\overline{P_S(x,t)}| = \left|\overline{\dfrac{\Delta \rho}{\rho_0}}\right| = 0$

and $\left|\overline{\dfrac{\Delta T}{100}}\right| = \left|\overline{\dfrac{\Delta R}{R_0(T_0)}}\right| = 0$, $|\overline{\Delta T}| = 0$K^0 and $\overline{|\Delta R|} = 0$cm .

With power input 0.1w/cm^2: $\left|\overline{\dfrac{P_S(x,t)}{P_0(T_0)}}\right| \approx 10^{-9}$, $\left|\overline{P_S(x,t)}\right| \approx 10^3 \text{dy/cm}^2$,

$\left|\overline{\dfrac{\Delta P}{P_0}}\right| \approx 10^{-12}$, $\left|\overline{\dfrac{\Delta T}{100}}\right| \approx \left|\overline{\dfrac{\Delta R}{R_0(T_0)}}\right| \approx 10^{-9}$, $\left|\overline{\Delta T}\right| \approx 10^{-7} \text{K}^0$ and $\left|\overline{\Delta R}\right| = 10^{-20} \text{cm}$.

5. Speed of Sound Formula for the Transition Metals

From 4.9 for $t \le 0$, an atom in the metal is confined to a volume $[2r_0 + R_0(T_0)]^3$, figure 4.6. $R_0(T_0)$ is determined at temperature T_0 at external pressure of one atmosphere.
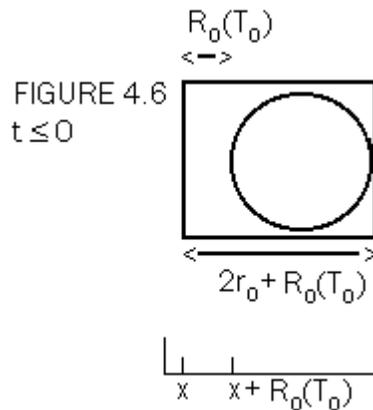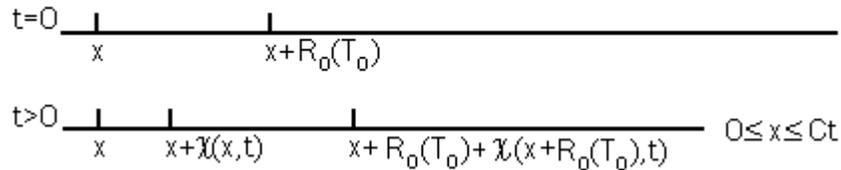

FIGURE 4.6
$t \le 0$

For $t \le 0$ one end of $R_0(T_0)$ is at x, figure 4.6, and the other end is at $x+R_0(T_0)$. For $t > 0$, for an atom within the sound field, figure 4.7, $R_0(T_0)$ becomes a function of x and t, $R(x,t)$, with $R(x,0)=R_0(T_0)$. From 4.1, $R(x,t)=d-2r_0$, where $R(x,t)$ is the mean distance atom #1 travels in the x direction between contact with atom #2 and contact with atom #3, averaged over one atomic period τ_A, figure 4.4. In general due to the sound field caused pressure $P_S(x,t)$; $R(x,t) \ne R_0(T_0)$. At time t, one end of $R(x,t)$ is at $x+\chi(x,t)$ and the other end is at $x+\chi(x,t)+R(x,t)$, figure 4.7. $\chi(x,t)$ is defined below.
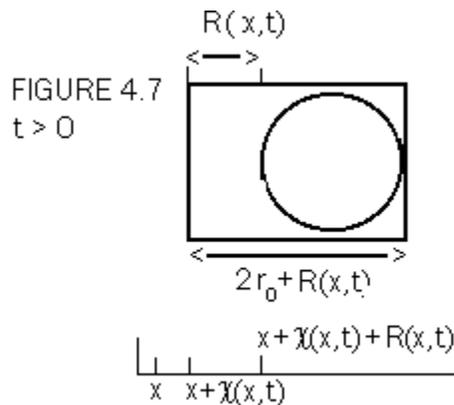
FIGURE 4.7
$t > 0$

At t=0 one end of $R_0(T_0)$ is at x and the other end is at $x+R_0(T_0)$: See figure 4.6 and line one of figure 4.8 . Figure 4.8 is not drawn to the same scale as figures 4.6 and 4.7.

FIGURE 4.8

Define the function $\chi(x,t)$ such that $\chi(x,0)=0$ and let $x+\chi(x,t)$ be the position of the x end of R(x,t) at time t. With $\chi(x+R_0(T_0),0)=0$; $x+R_0(T_0)+ \chi(x+R_0(T_0),t)$ is the position of the $x+R_0(T_0)$ end of R(x,t) at time t, figure 4.8 line two.

From figure 4.8: $R(x,t)=R_0(T_0)+ \chi(x+R_0(T_0),t)- \chi(x,t) \doteq R_0(T_0) [1+\frac{\partial \chi(x,t)}{\partial x}]$ and

$R(x,0)=R_0(T_0)$. $\Delta R(x,t)= R(x,t)- R(x,0) \doteq R_0(T_0)\frac{\partial \chi(x,t)}{\partial x}$. Using 4.10

4.12 $\qquad P_S(x,t)= -\left\{\frac{(C_p+3K)}{C_p}\right\}P_0\frac{\partial \chi(x,t)}{\partial x}$

Consider the forces produced by the sound wave across one atom. Figure 4.9. At x there is the sound caused force $P_S(x,t)\Delta A$ and at $x+2r_0+R(x,t)$, the sound caused force $P_S(x+2r_0+R(x,t),t)\Delta A$. The difference between these two forces,

FIGURE 4.9
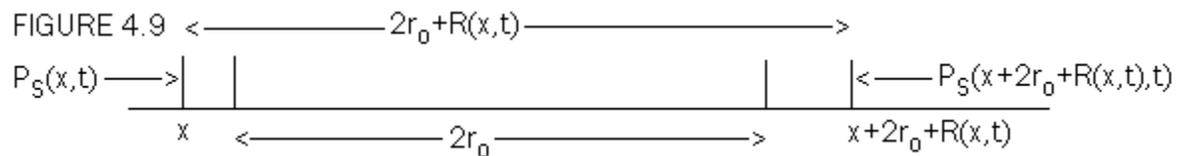
$[P_S(x+2r_0+R(x,t),t)- P_S(x,t)]\Delta A \doteq (2r_0+R) \frac{\partial P_S}{\partial x} \Delta A,$ is equal to the negative of the mass times the acceleration of the center of mass of the atom averaged over one period:

$(2r_0+R) \frac{\partial P_S}{\partial x} \Delta A = -P_0(2r_0+R)\Delta A\frac{\partial^2 \chi}{\partial t^2}$ and $\frac{\partial^2 \chi}{\partial t^2} = -\frac{1}{P_0} \frac{\partial P_S}{\partial x}$. Differentiate the last expression once with respect to x and differentiate 4.12 twice with respect to t. Solve both expressions for χ_{ttx} and equate.

4.13 $\qquad \frac{\partial^2 P_S}{\partial t^2}=\left\{\frac{(C_p+3K)}{C_p}\right\}\frac{P_0}{P_0}\frac{\partial^2 P_S}{\partial x^2}$

This is the wave equation and represents an adiabatic longitudinal sound wave pressure pulse traveling in the $\hat{x}$ direction with speed C_S given by:

$$4.14 \qquad C_S = \left\{ \frac{(C_p + 3K)}{C_p} \frac{P_o}{\rho_o} \right\}^{1/2} = \left[\frac{(C_p + 3K)}{C_p} \frac{2\mathring{r}_o KT}{mR_o(T)} \right]^{1/2}$$

4.14 can be evaluated using table 4.1 and the experimentally determined values for C_p: A sample calculation follows.

The experimentally determined value of the speed of sound C_{ex}, reference 3, chapter 4, for Al is $C_{ex_{Al}} = (6.4)10^5$cm/sec. Rounding off all values to two significant places and using $C_{p_{Al}} = 2.9K$, the theoretic value of $C_{S_{Al}}$ is:

$$C_{S_{Al}} = \left[\frac{(2.9+3)(2)(1.3)10^{-8}(1.4)10^{-16}(290)}{2.9 \quad (27)(1.7)10^{-24}(1.1)10^{-10}} \right]^{1/2} = (6.6)10^5 \frac{cm}{sec}$$

The C_S column of table 4.2 lists the theoretically derived adiabatic speed of sound and the C_{ex} column lists the experimentally determined speed of sound.

Table 4.2

Element	$C_S \frac{km}{sec}$	$C_{ex} \frac{km}{sec}$	$C_p \frac{}{K}$
Mg	6.6	5.8	3.0
Al	6.6	6.4	2.9
Ti	8.1	6.1	3.0
Fe	6.5	6.0	3.0
Ni	6.0	6.0	3.1
Cu	4.9	4.8	2.9
Zn	3.3	4.2	3.1
Mo	7.4	6.3	2.9
Ag	3.3	3.7	3.1
Sn	3.0	3.3	3.3
W	5.5	5.4	2.9
Pt	3.6	3.3	3.0
Au	2.7	3.2	3.0
Pb	1.8	2.0	3.3
U	3.5	3.4	3.4

The elements are listed in the order of increasing atomic mass. The good agreement between the theoretically derived value for adiabatic sound speed and the experimental value for sound speed gives credence to the idea that sound transmission in the transition metals is an adiabatic process.

6. The Bulk Modulus and the Speed of Sound in Solids

The isothermal bulk modulus B_Θ is defined by $B_\Theta = -V(\frac{dP_e}{dV})_\Theta$ where P_e is the total external pressure applied to a solid, liquid or gas sample. For an ideal gas, $P_e = \frac{NKT}{V}$, and under isothermal conditions, $(\frac{dP_e}{dV})_\Theta = -(\frac{P_e}{V})$ and:

4.15 $B_\Theta = -V(\frac{dP_e}{dV})_\Theta = P_e$:   Ideal Gas Case

Also $(\frac{dP_e}{d\rho})_\Theta = (\frac{P_e}{\rho})$ and $C_\Theta^2 = (\frac{dP_e}{d\rho})_\Theta = (\frac{P_e}{\rho}) = \frac{B_\Theta}{\rho}$ where C_Θ is the isothermal speed of sound. Therefore $B_\Theta = \rho C_\Theta^2$, however for O_2, N_2 and earth's atmosphere, the experimentally determined speed of sound C_{ex} is $C_{ex} = C_{adi} = (\gamma)^{\frac{1}{2}} C_\Theta$ where C_{adi} is the adiabatic speed of sound and $\gamma = \frac{C_p}{C_v}$, consequently:

4.16 $B_\Theta = \rho C_\Theta^2 = \rho C_{ex}^2 / \gamma$:   Ideal Gas Case

Although derived for an ideal gas, 4.16 was used in the second decade of the 19th century to experimentally determine B_Θ for the transition metals by measuring ρ and C_{ex} (The experimentally determined speed of sound in metals) and using $B_\Theta = \rho C_{ex}^2 / \gamma$.

For the transition metals $\gamma = \frac{C_p}{C_v} \doteq (3K/1.5K) = 2$.

As an example: $B_{Fe_\Theta} = \frac{(7.9)}{(2.0)}[(6.0)10^5]^2 = (1.4)10^{12} dy/cm^2$. The experimentally determined value is: $B_{Fe_{ex}} = (1.7)10^{12} dy/cm^2$. See reference 4, chapter 4.

Subsequent experimentalists in the twentieth century directly determining B_Θ by direct compression of a metal slug, thus had the target value $\rho C_{ex}^2 / \gamma$ to aim for.

In order that $-V(\frac{dP_e}{dV})_\Theta = P_e$, it is necessary and sufficient that $P_e(T_0)V(T_0) = Const$. Therefore in order that $B_\Theta = P_e$, it is necessary and sufficient that $P_e(T_0)V(T_0) = Const$. Clearly $P_e(T_0)V(T_0) = Const$. does not hold for a transition metal and therefore $B_\Theta \neq P_e$ for a transition metal and consequently $B_\Theta \neq \rho C_{ex}^2 / \gamma$.

Note that for a gas in equilibrium, the total internal pressure P_T equals the total external pressure P_e: $P_T = P_e$. For a solid metal in equilibrium, the total internal pressure P_T does not equal the total external pressure P_e: $P_T \neq P_e$ although $\Delta P_T = \Delta P_e$. For example a solid in vacuum has an external pressure $P_e = 0$ and an internal pressure $P_T \neq 0$.

In the following, the theoretic value of the bulk modulus $B_{\Theta_{Th}}$ will be derived from the equation of state derived in section 3: $P_T V = \dfrac{(2r_0 + R)}{R} NKT$. Using $\left(\dfrac{dP_T}{dV}\right)_\Theta = \left(\dfrac{dP_e}{dV}\right)_\Theta$,

$V = (2r_0 + R)^3$, $dV = 3(2r_0 + R)^2 dR$, $r_0 \approx 10^{-8} cm$ and $R \approx 10^{-11} cm$: $B_{\Theta_{Th}} = -V\left(\dfrac{dP_e}{dV}\right)_\Theta = -V\left(\dfrac{dP_T}{dV}\right)_\Theta =$

$-V\left[\left(\dfrac{\partial P_T}{\partial R}\right)_{\Theta, V}\dfrac{dR}{dV} + \left(\dfrac{\partial P_T}{\partial V}\right)_{\Theta, R}\right] = P_T V\left[\dfrac{1}{3R(2r_0 + R)}2 + \dfrac{1}{(2r_0 + R)}3\right] = \dfrac{2r_0}{3R}(1 + 2R/r_0)P_T \doteq \dfrac{2r_0}{3R}P_T$.

Also, $P_T = \dfrac{KT}{R(2r_0 + R)^2} \doteq \dfrac{KT}{R(2r_0)^2}$ and consequently $B_{\Theta_{Th}} = \dfrac{(2r_0)^3 P_T^2}{3KT}$.

Define the applied pressure P_A as $P_A \equiv P_T - P_0$. P_A replaces the symbol P_S of sections 4 and 5. A replacement symbol for P_S is needed as in general $P_A >> 10^6 dy/cm^2$ while in general $P_S << 10^6 dy/cm^2$. With $P_T^2 = P_0^2(1 + P_A/P_0)^2$, most experimental determinations of $B_{\Theta_{Ex}}$ have $P_A \lesssim 10^{10} << 10^{12} \approx P_0 dy/cm^2$ and therefore

$P_T^2 = P_0^2(1 + 2P_A/P_0)$. Also $P_0 \doteq \dfrac{KT}{R_0(T)(2r_0)^2}$ and $B_{\Theta_{Th}}$ becomes:

4.17   For a Transition Metal $B_{\Theta_{Th}} = \dfrac{2r_0}{3R_0(T_0)}P_0^2(1 + 2P_A/P_0)$

$B_{\Theta_{Th}} \approx \dfrac{10^{-8}10^{12}}{10^{-11}} = 10^{15} \ dy/cm^2$. Using 4.7 , table 4.1 and the case $P_A << P_0$:

$B_{Fe_{\Theta_{Th}}} = \dfrac{2r_0 P_0}{3R_0(T_0)} = \dfrac{0.67(1.1)10^{-8}(1.7)10^{12}}{(4.6)10^{-11}} = (2.7)10^{14} dy/cm^2$

$B_{\Theta_{Th}}$ can also be written as a function of sound speed. Using 4.14:

4.18   For a Transition Metal $B_{\Theta_{Th}} = \dfrac{2r_0}{3R_0(T)}(1 + 2P_A/P_0)\left(\dfrac{C_p}{C_p + 3K}\right)P_0 C_S^2$

$\doteq \dfrac{2r_0}{3R_0(T)}(1 + 2P_A/P_0)P_0 C_S^2 \dfrac{}{\gamma}$

$B_{\Theta_{Ex}}$ has been directly determined by compressing a metal slug isothermally in an enclosed pressure cell and measuring the change of length ΔL as a function of applied pressure. The metal slugs used in the determination, Reference 4, chapter 4, are right circular cylinders 1.9cm in length by .51cm in diameter. For example: a Fe slug at an applied pressure of $(2.9)10^{10}$dy/cm^2 is compressed in the ratio

$(-\Delta L/L_o)_{Fe_{\Theta_{ex}}} = (.017)/3 = (5.7)10^{-3}$ with $(-\Delta L)_{Fe_{\Theta_{ex}}} = (1.9)(5.7)10^{-3} = (1.1)10^{-2}$cm.

i.e. at an applied pressure of $P_A = (2.9)10^{10}$dy/cm^2 an iron cylinder 1.9cm in length

by .51cm in diameter decreases in length by $(1.1)10^{-2}$cm. The experimentally

determined isothermal bulk modulus $B_{\Theta_{Ex}} = -V(\frac{dP}{dV})_T \doteq -V(\frac{\Delta P}{\Delta V})_T = -(2r_o+R)^3(\frac{1}{3(2r_o+R)^2}2\frac{\Delta P}{\Delta R})_T =$

$-\frac{(2r_o+R)}{3}(\frac{\Delta P}{\Delta R})_T$ and with $(-\Delta L/L_o)_{Fe_{\Theta_{ex}}} = -\frac{\Delta R}{(2r_o+R)} = (.017)/3$, $B_{\Theta_{Ex}}$ becomes:

$B_{Fe_{\Theta_{Ex}}} \doteq -\frac{(2r_o+R)}{3}(\frac{\Delta P}{\Delta R})_T = \frac{(2r_o+R)(2.9)10^{10}(3)}{3(.017)(2r_o+R)} = (1.7)10^{12}$dy/cm^2

The basic measurement $(-\Delta L)_{ex}$, is made by measuring the electrical resistance in a Nirex wire between the point of attachment on the specimen and a fixed point on the pressure casing: Once at $P_A = 0$ dy/cm^2 and again at $P_A = (2.9)10^{10}$dy/cm^2. Given the target formula 4.16 and the difficulty in making consistent electric resistance measurements at high pressure, it is understandable that human error may account for the partial agreement between the experimentally determined

$B_{Fe_{\Theta_{Ex}}} = (1.7)10^{12}$dy/cm^2, and the B_{Fe_Θ} computed from the target formula 4.16,

i.e. $B_{Fe_\Theta} = (1.4)10^{12}$dy/cm^2

The theoretic value of $(-\Delta L/L_o)_{\Theta_{Th}}$ is:

$(-\Delta L/L_o)_{\Theta_{Th}} = -\frac{(2r_o+R)-(2r_o+R_o)}{(2r_o+R_o)} \doteq -\frac{\Delta R_\Theta}{(2r_o+R_o)} \doteq -\frac{\Delta R_\Theta}{2r_o} = \frac{R_o(T)P_A}{2r_oP_o}$

Evaluating $(-\Delta L/L_o)_{\Theta_{Th}}$ for the Fe slug using 4.7 and table 4.1:

$(-\Delta L/L_o)_{Fe_{\Theta_{Th}}} = \frac{R_o(T)P_A}{2r_oP_o} = \frac{(4.6)10^{-11}(2.9)10^{10}}{(2.2)10^{-8}(1.7)10^{12}} = (3.5)10^{-5}$ and

$(-\Delta L)_{Fe_{\Theta_{Th}}} = (1.9)(3.5)10^{-5} = (6.7)10^{-5}$cm. Which figure is correct, the experimentally

determined value, $(-\Delta L)_{Fe_{\Theta_{Ex}}} = (1.1)10^{-2}$cm or the theoretically determined value,

$(-\Delta L)_{Fe_{\Theta_{Th}}} = (6.7)10^{-5}$cm, can be determined by direct measurements taken from x-

ray photographs. One photograph taken at $P_A=0$ dy/cm^2 and another taken at $P_A=(2.9)10^{10}$dy/cm^2.

7. Average Contact Time $\overline{\Delta t_C}$

In section 3 in order to derive the equation of state 4.6, it was hypothesized that $\overline{\Delta t_C}<<R_0(T)/[\frac{KT}{2\pi m}]^{\frac{1}{2}}$. In particular evaluating the inequality for Fe yields, $\overline{\Delta t_{C_{Fe}}}<<(5.5)10^{-15}$sec. The consequences of this hypothesis are examined below.

Consider two isolated identical atoms #1 and #2 . The coordinate frames in Figure 4.10 are at rest with respect to the center of mass of atoms #1 and #2 and are therefore inertial frames. Ignore for the moment the effects of the interaction potential Φ_{12} between the two atoms i.e. Φ_{12} is set at $\Phi_{12}\equiv 0$. At t=0, see figure 4.10A , atom #1 with momentum $+mU\hat{x}$, collides with atom #2 with momentum $-mU\hat{x}$. Figure 4.10B shows atoms #1 and #2 during collision and Figure 4.10C

FIGURE 4.10
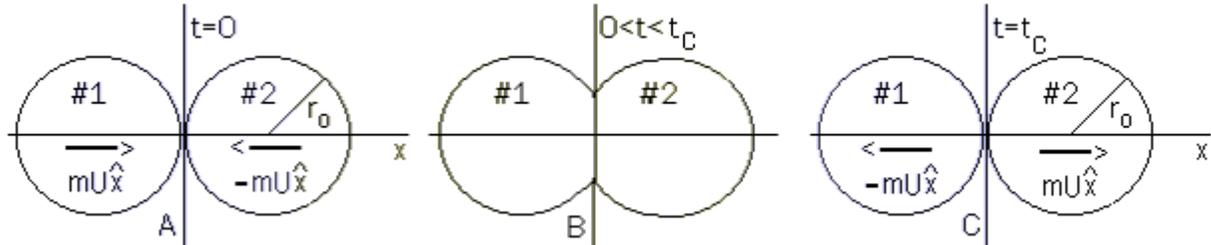
shows atoms #1 and #2 at the instant of separation.

During the time interval $0\leq t\leq t_C$, atoms #1 and #2 compress one another changing translational kinetic energy into vibrational kinetic energy plus atomic field potential energy then the process reverses itself and vibrational kinetic energy is changed into translational kinetic energy plus atomic field potential energy.
The position of mass points within atom #2 is given by $\underset{\sim}{h}=\underset{\sim}{x}+\underset{\sim}{\chi}(\underset{\sim}{x},t)$ where $\underset{\sim}{\chi}(\underset{\sim}{x},0)=0$ and $(x-r_0)^2+y^2+z^2\leq r_0^2$. The velocity is $\underset{\sim}{\dot{h}}=\underset{\sim}{\dot{\chi}}(\underset{\sim}{x},t)$ and is split into two components, $\underset{\sim}{\dot{\chi}}(\underset{\sim}{x},t)_{vb}$, the vibrational part of $\underset{\sim}{\dot{\chi}}$ where $\overline{\underset{\sim}{\dot{\chi}}(\underset{\sim}{x},t)_{vb}}=0$ for $0\leq t\leq t_C$ and $\underset{\sim}{\dot{\chi}}(\underset{\sim}{x},t)_{Tr}$, the translational part of $\underset{\sim}{\dot{\chi}}$ where $\overline{\underset{\sim}{\dot{\chi}}(\underset{\sim}{x},t)_{Tr}}\neq 0$, over the same time interval $0\leq t\leq t_C$.

More precisely, for every mass point in atom #2 with coordinates $\underset{\sim}{h}$, there is a time τ,

$0 \leq \tau \leq t_C$ such that $\dot{\underset{\sim}{\chi}}(\underset{\sim}{\chi},\tau)_{Tr}=0$ and $\dot{\underset{\sim}{\chi}}(\underset{\sim}{\chi},t)_{Tr}\hat{\underset{\sim}{\chi}}< 0$ for t<τ and $\dot{\underset{\sim}{\chi}}(\underset{\sim}{\chi},t)_{Tr}\hat{\underset{\sim}{\chi}} > 0$ for t>τ.

The original assumption restated here is that $\overline{\Delta t_C}<<R_0(T)/[\frac{KT}{2\pi m}]^{\frac{1}{2}}$.

Consider the acceleration of an elemental sphere of atomic material, Figure 4.11, held together by atomic field forces and kept from collapse by elastic contact collisions of elemental parts of the sphere with one another.

FIGURE 4.11
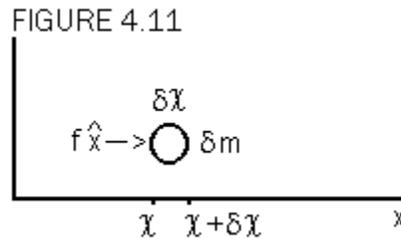
Classically if a force $f\hat{\underset{\sim}{\chi}}$ is applied as indicated, the entire sphere moves instantaneously according to $f\hat{\underset{\sim}{\chi}}=\delta m\ddot{\underset{\sim}{\chi}}\hat{\underset{\sim}{\chi}}$. However under the influence of the applied force, the sphere will be compressed, the internal vibration rate will increase and the effects of the applied force will not be felt at all points in the sphere at the same time. To therefore calculate the effects of an applied force on the sphere necessitates knowing the effects of the applied force on the elemental, vibrating parts of the sphere. This problem is discussed in chapter 5, section 4 and chapter 6, section 4.

8. Thermal conductivity

Consider two heat reservoirs, one at temperature T_1 at x=0 and the other at T_2 at x=L, figure 4.12. A transition metal wire of length L and cross section A(x) is placed between the two reservoirs. Heat energy flows through the metal, heating one reservoir and cooling the other. Two cases are considered: 1. T(x), the temperature along the metal bar, is independent of time, 2. T(x,t) is time dependent. In this case, the temperature of the heat source and sink is also time dependent.

FIGURE 4.12
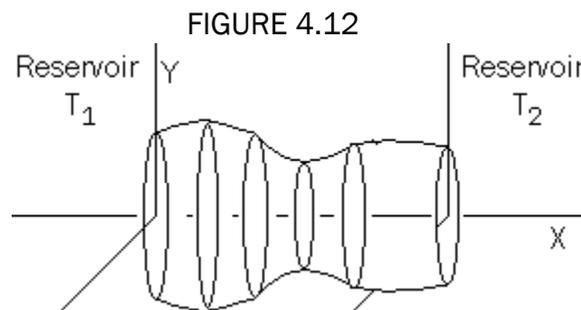
Let $\underset{\sim}{\Phi}=\Phi_1\hat{x}+\Phi_2\hat{y}+\Phi_3\hat{z}$ represent the energy flux, where $\Phi_1\hat{x}$ is the energy per unit time crossing a unit area perpendicular to the $\hat{x}$ direction. $\Phi_2\hat{y}$ and $\Phi_3\hat{z}$ have similar definitions. Generally $|\underset{\sim}{\Phi}|$ is measured in watts/cm^2. We will consider A to be independent of x, A=const., so that the energy flux is $\underset{\sim}{\Phi}(x) = \Phi_1(x)\hat{x}$.

Consider three atoms in the metal bar, figure 4.13. The S_2 plane is at x and the S_1 plane is at $x+2r_0+R_0[T(x)]\equiv x+\Delta x$. Let the temperature of atom #1 after its collision with atom #3 on the S_2 plane at mean position x and before its collision with atom

#2 on the S_1 plane be T(x), where $\frac{1}{2}mU^2_{rms}(x)=\frac{3}{2}KT(x)$ and where $U^2_{rms}(x)$ is the root mean square speed squared of atom #1 after collision with atom #3 and before collision with atom #2. The temperature of atom #1 after its collision with

FIGURE 4.13
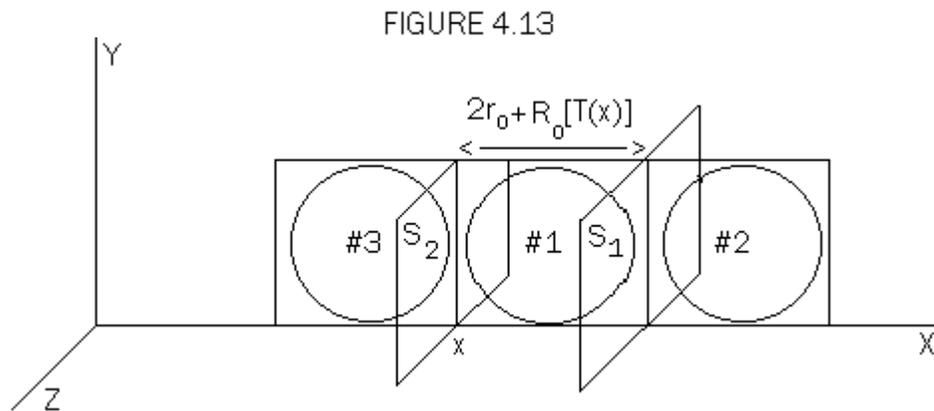
atom #2 on the S_1 plane at mean position $x+2r_0+R_0[T(x)]$ is

$T(x+2r_0+R_0[T(x)])\equiv T(x+\Delta x)$, where $\frac{1}{2}mU^2_{rms}(x+\Delta x)=\frac{3}{2}KT(x+\Delta x)$ and where $U^2_{rms}(x+\Delta x)$ is the root mean square speed squared of atom #1 after collision with atom #2 and before collision with atom #3. The change in translational kinetic energy of atom #1 is

$\Delta E=\frac{3}{2}[KT(x+\Delta x)-KT(x)]$. In a monatomic gas at constant volume,

$\Delta E=C_V\Delta T-\Delta\varepsilon_{ph}=\frac{3}{2}K\Delta T+m\Delta C_1-\Delta\varepsilon_{ph}$ where $\Delta\varepsilon_{ph}$.is the total energy needed to create photons by 1 atom in the time interval during which ΔT is measured and $m\Delta C_1$ is the change in internal energy of the atom. In an unconstrained solid, $\Delta E=C_p\Delta T_p-P_{ex}\Delta V_p$.

$-\Delta\varepsilon_{ph}$ is not included as photons are only created by atoms on the surface of the solid. In appendix 4A it is shown that $|-P_{ex}\Delta V_p|<<|C_p\Delta T_p|$.

The energy flux $\Phi_1\hat{x}$ becomes:

$$\Phi_1=-\frac{\Delta E}{\Delta t\,\Delta A}=-\frac{C_p\Delta T}{\Delta t\,\Delta A}=-\frac{C_p\Delta T}{\Delta t\,\Delta x^2}\doteq-\frac{C_p\frac{dT}{dx}}{\Delta t\,\Delta x} \text{ and } \Phi_1\doteq-\frac{C_p\frac{dT}{dx}}{\Delta t\,\Delta x}.$$

$\bar{U}_{x>0}$ is the average speed of an atom in the positive x direction averaged over all atoms in the metal wire with velocities in the positive x direction and at temperature T(x): $\bar{U}_{x>0} = (\frac{KT(x)}{2\pi m})^{1/2}$, reference 5, chapter 4. $\bar{U}_{x<0}$ is the average speed of an atom in the negative x direction averaged over all atoms in the metal bar with velocities in the negative x direction and at temperature T(x+Δx):

$\bar{U}_{x<0} = (\frac{K T(x+\Delta x)}{2\pi m})^{1/2}$. With $\Delta x \doteq 2r_0 \cdot 10^{-8}$cm: T(x)$\doteq$T(x+$\Delta$x). i.e. as an extreme example with $\frac{\Delta T}{\Delta x} = 10^4 (\frac{K^0}{cm})$ it follows that $\frac{\Delta T}{\Delta x}(2r_0) = T(x+\Delta x) - T(x) = 2 \cdot 10^{-4}(K^0)$ and for

T(x)$>> 2 \cdot 10^{-4} \Rightarrow$ T(x)$\doteq$T(x+Δx) and $\bar{U}_{x>0} \doteq \bar{U}_{x<0}$.
With $\Delta t = \Delta t_1 + \Delta t_2$, $\bar{U}_{x>0} \cdot \Delta t_1 + \bar{U}_{x<0} \cdot \Delta t_2 = \bar{U}_{x>0} \cdot (\Delta t_1 + \Delta t_2) = \bar{U}_{x>0} \cdot \Delta t = 2R(x)$ and with

$\Delta x \doteq 2r_0$, Φ_1 becomes: $\Phi_1 = -\frac{C_p}{4r_0 R(X)}(\frac{KT(x)}{2\pi m})^{1/2} \cdot \frac{dT}{dx}$. The coefficient of thermal

conductivity K_T is defined as the negative of the coefficient of $\frac{dT}{dx}$ i.e.

$K_T = \frac{C_p}{4r_0 R(X)}(\frac{KT(x)}{2\pi m})^{1/2}$. Restricting attention to uniform cross sectional area

A=const., then $\Phi_1 = -K_T\frac{dT}{dx}$=const. In the following it is not assumed that K_T is a constant. Compiling results at this point:

4.19 $\Phi_1 = -K_T\frac{dT}{dx}$=const., $K_T = \frac{C_p}{4r_0 R(X)}(\frac{KT(x)}{2\pi m})^{1/2}$, uniform cross sectional area

It will not do to experimentally determine T(x) and R(x) and substitute the values of

T(x) and R(x) in $\frac{C_p}{4r_0 R(X)}(\frac{KT(x)}{2\pi m})^{1/2}$ in order to determine K_T. One must experimentally

determine Φ_1 and $\frac{\Delta T}{\Delta x} \doteq \frac{dT}{dx}$ and using $K_T = -\frac{\Phi_1}{\frac{\Delta T}{\Delta x}}$, experimentally verify that

$\frac{\Phi_1}{\frac{\Delta T}{\Delta x}} \doteq \frac{C_p}{4r_0 R[T(x)]}(\frac{KT(x)}{2\pi m})^{1/2}$.

Table 4.1 lists computed values of R=R(T) under conditions of 0 heat flow. For the sake of exposition, compute K_T for Al, Ag, and Pb using table 4.1 interpolated for 300^{0}K. For Al,

$K_T = [\frac{C_p}{4r_0 R(X)}(\frac{KT(x)}{2\pi m})^{1/2}] = \frac{2.9(1.4) \cdot 10^{-16}}{4(1.3) \cdot (1.1) 10^{-18}}(\frac{1.4 \cdot 10^{-14} \cdot 3}{2\pi (4.6) \cdot 10^{-23}})^{1/2} = 8.5 \cdot 10^5 \frac{erg}{sec.cm^0 K}$

$= 8.5 \cdot 10^{-2} \frac{w}{cm^0 K}$

Table 4.3 lists the theoretic value for K_T computed using formula 4.19 above and the experimental value $K_{T_{ex}}$ determined at 300^oK . See reference 6, chapter 4.

Table 4.3

Element	$K_T(w/cm^oK)$	$K_{T,ex}(w/cm^oK)$	$\frac{K_{T,ex}}{K_T} \equiv a_o$
Al	$8.5 \cdot 10^{-2}$	2.4	28
Ag	$4.4 \cdot 10^{-2}$	4.3	98
Pb	$1.4 \cdot 10^{-2}$	$3.5 \cdot 10^{-1}$	25

The agreement between the theoretic value and the experimental value is not good. The theoretic value is between 1 and 2 orders of magnitude smaller than the experimental value.

It is hypothesized that the difference in mean kinetic energy between adjacent atoms in the x direction, is carried as a surface percussive wave followed by a surface shear wave. The two waves spread out over the surface of atom #1 (fig. 4.13 and 4.14) Starting from the contact point (Called CP_1) between atoms #1 and #3 and reconverging at the contact point (CP_2) between atoms #1 and #2. The bulge at CP_2 is approximated by a cone of volume $V=\frac{1}{3}\pi R_o^2 h=\frac{1}{3}\pi R_o^2 \Delta r_o$. The energy $E_{\Delta r}$ to increase the radius of the atom by Δr_o is: $E_{\Delta r}\frac{\pm m^2 H}{r_o^2}\Delta r_o$ and for small enough R_o and Δr_o the energy to form a bulge at CP_2 of volume $V_B=\pi R_o^2 \Delta r_o$ is $E_B\frac{\pm m^2 H}{r_o^2}\Delta r_o(\frac{\theta}{2\pi})$, θ in radians.

We wish to find the dimensions of the conical bulge R_o and Δr_o. With $a_o\equiv\frac{K_{T,ex}}{K_T}=\frac{R(x)}{R'(x)}$

Where $K_T=\frac{C_p}{4r_o R(X)}(\frac{KT(x)}{2\pi m})^{1/2}$ and $K_{T,ex}=\frac{C_p}{4r_o R'(x)}(\frac{KT(x)}{2\pi m})^{1/2}$. Using fig.4.14, $R(x)=2\Delta r_o+R'(x)$

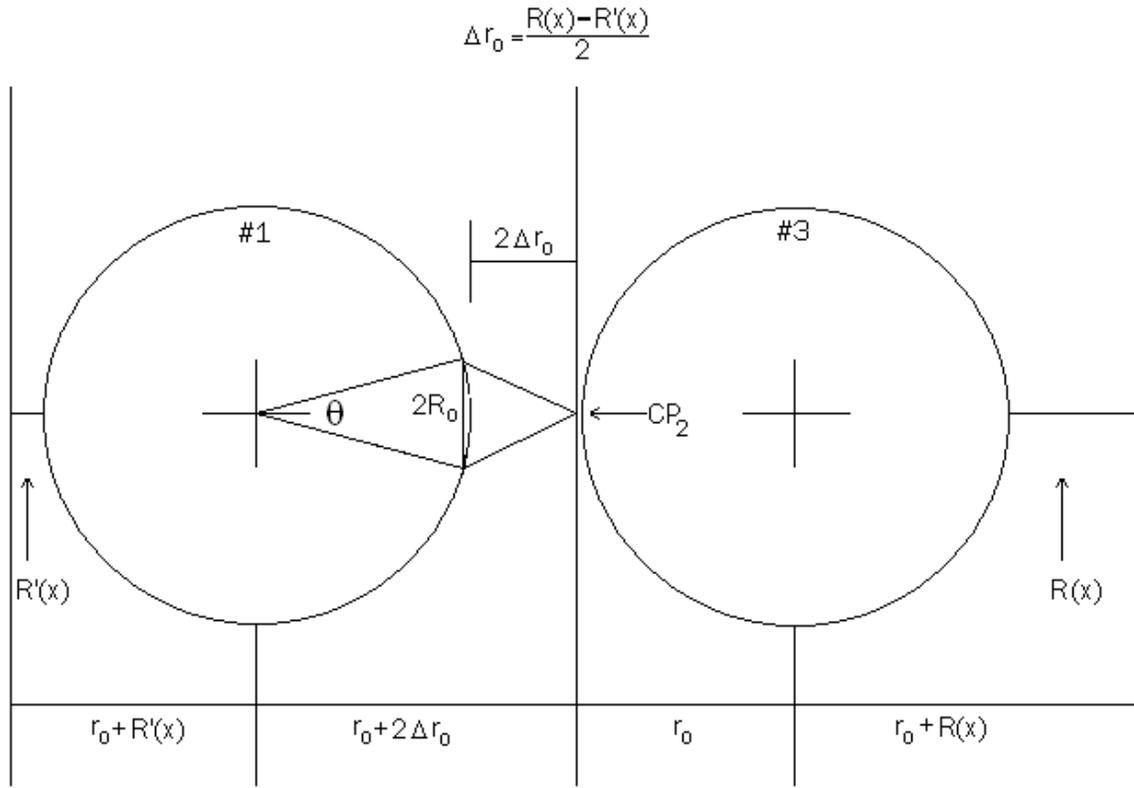and $\Delta r_o=(\frac{a_o-1}{2a_o})R(x)$ and $E_B\frac{\pm m^2 H}{r_o^2}(\frac{a_o-1}{2a_o})R(x)(\frac{\theta}{2\pi})$.

The energy E_{cb} to form a conic bulge with volume $V=\frac{1}{3}\pi R_o^2 \Delta r_o$ is $E_{cb}=\frac{1}{3}E_B\frac{\pm 1}{3}\frac{m^2 H}{r_o^2}(\frac{a_o-1}{2a_o})R(x)(\frac{\theta}{2\pi})$.

Define the down and back time Δt_{db} for an atom as $\Delta t_{db}=\frac{2R'(x)}{\overline{U}_{x>o}}=\frac{2R(x)}{a_o\overline{U}_{x>o}}=\frac{2R(x)}{a_o}(\frac{KT(x)}{2\pi m})^{-\frac{1}{2}}$.

Setting $E_{cb}=-K_{T,ex}\frac{dT}{dx}\Delta t_{db}\Delta A=-K_{T,ex}\frac{dT}{dx}(\frac{2R(x)}{a_o})[(\frac{KT(x)}{2\pi m})^{-\frac{1}{2}}](2r_o)^2\frac{\pm 1}{3}\frac{m^2 H}{r_o^2}(\frac{a_o-1}{2a_o})R(x)(\frac{\theta}{2\pi})$

FIGURE 4.14

$$\Delta r_0 = \frac{R(x) - R'(x)}{2}$$

$$2\Delta r_0$$

#1   #3

$$\theta \quad 2R_0 \quad \leftarrow CP_2$$

R'(x)   R(x)

$$r_0 + R'(x) \qquad r_0 + 2\Delta r_0 \qquad r_0 \qquad r_0 + R(x)$$

Solve for θ yielding, $\theta = -24\pi(\frac{a_0}{a_0-1})(\frac{r_0^3}{m^2 H})\frac{C_p}{R(x)}\frac{dT}{dx}$. For future use for a conductor with uniform cross section:

4.20 $\Delta r_0 = (\frac{a_0-1}{2a_0})R(x)$, $\theta = -24\pi(\frac{a_0}{a_0-1})(\frac{r_0^3}{m^2 H})\frac{C_p}{R(x)}\frac{dT}{dx}$, $2R_0 = 2r_0\tan\frac{\theta}{2}$

Values for Δr_0, θ and $2R_0$ have been computed for Al, Ag and Pb and are given in table 4.4 using a_0 from table 4.3. An interpolated value of $R(x(T))$ evaluated at $T = 400°K$ has been computed using table 4.1 and $R'(x(T))$ has been computed using $R'(x(T)) = R(x(T)) - 2\Delta r_0$. During the time interval from the onset of heat flow until heat flow reaches its steady state value at $\underset{\sim}{h}(x,t) = \{x + \chi(x,t)\}\hat{x}$ for some τ, $t = \tau$, the average distance that an atom at x travels between collisions in the x direction decreases from $R(h(x,o))$ to $R'(h(x,t))$, $t \geq \tau$. This can be experimentally verified by measuring the speed of sound in the material as a function of time. At $400°K$ with no heat flow and using 4.14, the speed of sound in Al is $6.6 \frac{km}{sec}$ and at $400°K$ with heat flow under the above conditions the speed of sound is:

$$C_{Al} = 2[\frac{(1.3)10^{-8}(1.4)10^{-16}400}{(4.6)10^{-23}(5.4)10^{-12}}]^{\frac{1}{2}} = 34 km/sec.$$

Table 4.4, T=400°K

Element	R(cm)	R'(cm)	Δr_0(cm)	$\frac{dT}{dx}(\frac{K^0}{cm})$	θ(deg)	$2R_0$(cm)
Al	$1.5 \cdot 10^{-10}$	$5.4 \cdot 10^{-12}$	$7.3 \cdot 10^{-11}$	-1	$1.1 \cdot 10^{-11}$	$2.6 \cdot 10^{-21}$
Al	$1.5 \cdot 10^{-10}$	$5.4 \cdot 10^{-12}$	$7.3 \cdot 10^{-11}$	-10	$1.1 \cdot 10^{-10}$	$2.6 \cdot 10^{-20}$
Al	$1.5 \cdot 10^{-10}$	$5.4 \cdot 10^{-12}$	$7.3 \cdot 10^{-11}$	-10^2	$1.1 \cdot 10^{-9}$	$2.6 \cdot 10^{-19}$
Ag	$1.5 \cdot 10^{-10}$	$1.5 \cdot 10^{-12}$	$7.5 \cdot 10^{-11}$	-1	$8.1 \cdot 10^{-13}$	$1.8 \cdot 10^{-22}$
Ag	$1.5 \cdot 10^{-10}$	$1.5 \cdot 10^{-12}$	$7.5 \cdot 10^{-11}$	-10	$8.1 \cdot 10^{-12}$	$1.8 \cdot 10^{-21}$
Ag	$1.5 \cdot 10^{-10}$	$1.5 \cdot 10^{-12}$	$7.5 \cdot 10^{-11}$	-10^2	$8.1 \cdot 10^{-11}$	$1.8 \cdot 10^{-20}$
Pb	$3.0 \cdot 10^{-10}$	$1.2 \cdot 10^{-11}$	$1.4 \cdot 10^{-10}$	-1	$2.0 \cdot 10^{-13}$	$2.0 \cdot 10^{-23}$
Pb	$3.0 \cdot 10^{-10}$	$1.2 \cdot 10^{-11}$	$1.4 \cdot 10^{-10}$	-10	$2.0 \cdot 10^{-12}$	$2.0 \cdot 10^{-22}$
Pb	$3.0 \cdot 10^{-10}$	$1.2 \cdot 10^{-11}$	$1.4 \cdot 10^{-10}$	-10^2	$2.0 \cdot 10^{-11}$	$2.0 \cdot 10^{-21}$

The predicted sound speed at 400°K during heat flow is some 5.2 times faster than during no heat flow at 400°K and can be measured in order to confirm or deny atomic radial expansion during heat flow. Similar calculations can be performed for the other transition metals.

In reality the temperature in the material during heat flow is not uniform and the average speed of sound in the material must be computed using 4.14 and then compared with the experimentally determined value.

In 4.19, Φ_2 and Φ_3, the energy flux in the y direction and the z direction are respectively: $\Phi_2 = \Phi_3 = 0$. In general:

4.21 $\quad \underset{\sim}{\Phi} = -K_T \nabla T$, $\quad K_T = \left[\frac{C_p}{4\alpha r_0} \left(\frac{K}{2\pi mT(\underset{\sim}{x})} \right)^{1/2} \right]$

If the temperature in the metal bar is time dependent, K_T becomes:

4.22 $\quad K(t)_T = \left[\frac{C_p}{4\alpha r_0} \left(\frac{K}{2\pi mT(\underset{\sim}{x},t)} \right)^{1/2} \right]$ $\quad K(t)_T$ is the time dependent thermal conductivity.

9. Appendix 4A

To show that $|-P_{ex} \Delta V_p| << |C_p \Delta T_p|$; Where $P_{ex} = 10^6 \frac{dy}{cm}2$, $V_p = (2r_0 + R_p)^3$, and

$|-P_{ex} \Delta V_p| = 3 \cdot 10^6 \cdot (2r_0 + R)^2 \Delta R_p \doteq 10^7 \cdot 10^{-16} \cdot \Delta R_p$. With $\alpha = $ const. and given that

$R_p \doteq \alpha T$: Using table 4.1, $\alpha \approx 10^{-12} (\frac{cm}{{}^0 K})$ and $|-P_{ex} \Delta V_p| \approx 10^{-21} \cdot |\Delta T_p| << 10^{-16} \cdot |\Delta T_p| \doteq |C_p \Delta T_p|$

Q.E.D.

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